

**PROJECT 325A**  
**SUMMARY REPORT**

**PERIOD:** December 1, 1971 to December 31, 1971

**Submitted By:**

[Redacted]

**Project Manager**

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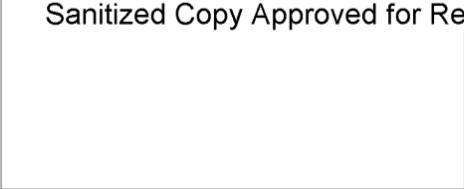
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SUMMARY

December saw the continuation of project effort on test pilot coating runs of the 325A formulation. AEI speeds of 2.3 were realized on two separate coating trials. Associated with these speeds were the required sensitometric, resolution and spectral sensitivity parameters. The nonavailability of a roll red light processor and solvent fixer posed severe processing problems in handling the 6.6" web in the 30 foot test lengths.

A complete briefing was put together covering the project progress from October 1969 through December 1971. A technical proposal and costing for continuation of this project is underway with briefing and proposal to be delivered at the customer facility January 7, 1972.

The ninety day effort, completed December 31, 1971, has shown the ability to transfer the hand coated formulations to pilot coatings. No improvement in shelf life was realized beyond what was found with the hand coated formulations. This is believed to be due in large part to the inability to setup special drying conditions on the pilot coater because of its present design.

In-depth work on chemical impurities as a factor in shelf life/speed decay was continued.

Isolation of a major impurity in D260 has been accomplished. Identification of this impurity is underway. Several experiments were run in the last week of December in which the isolated impurity was introduced into the coating solution just prior to coating. The result was sensitometric values which closely approximates the properties of a 45-60 minute old film.

## 1.0 CHEMICAL R and D

### Materials' Purification and Synthesis

#### D260:

Success was realized in preparing additional quantities of photograde D260 by December 10th, three days ahead of schedule. Sufficient D260 (188.1 g) was made available to complete the pilot coating effort and to sustain the research effort through the early part of January.

In response to the D260 shortage, several experiments were carried out to purify unacceptable D260: hydrogenation with and without palladium catalyst, and extraction with hydrochloric acid. These methods were not successful in removing the impurity.

The purification of D260 continues as a problem. It appears that D260 made in this laboratory can be consistently purified to photograde material with 50-60% yield, based on crude material. However, our subcontractor's samples have stubbornly resisted purification because of a far larger proportion of an impurity which has been identified as the principal culprit in photoinferior material. This impurity has been isolated by repeated recrystallizations. The compound has a melting point of 194-196°C and reacts with carbon tetrabromide in benzene to give a deep orange solution followed by precipitation of an orange solid. The infrared spectrum of the material most nearly corresponds to that of leuco crystal violet. The spectrum indicates there is no bridgehead present as in D260. Samples have been sent out for carbon, hydrogen, nitrogen, oxygen analyses; molecular weight determination, mass spectral analysis, and NMR analysis.

Another impurity has been detected by thin layer chromatography (TLC). It appears to be absent in material obtained from the subcontractor, but is present in considerable quantity in material synthesized in-house. It is present in photograde material so that it cannot be the cause of photoinferiority as is the other impurity described above. Attempts are underway to isolate and identify this impurity. Its presence suggests that current photograde material may be less than optimum, and there is also the question of its relationship to speed decay.

Work continues in order to purify more D260 for support of the continuing research effort.

**CB<sub>4</sub>:**

Successful purification of photograde CB<sub>4</sub>, both by recrystallization of Freeman crude and sublimation of BDH, continued without incident. A total of 2,235 g of photograde material was consumed in pilot coatings during December.

An additional 5 kg of crude BDH CB<sub>4</sub> has been received. This material is still sealed and will be initially exposed only to a highly purified air atmosphere. The purpose will be to establish environmental contamination as the cause for deterioration of this material. This study is scheduled for the latter part of January.

Another prime source of CB<sub>4</sub> has been located, and 5 kg ordered from Koch-Light Laboratories in England. This material should arrive in January. At the 1000 kg level, Koch-Light has quoted \$18.75/kg FOB London Airport.

**D7:**

A total of 119.9 g of D7 was consumed in pilot coatings during December. Over 500 g remain in stock, and there is no plan to synthesize more D7 in the immediate future.

**N-oxides:**

Twenty-seven amine oxides, nearly all of which have been procured from commercial sources, have been carefully purified and dried.

**Air Sampling:**

A large air sampling program was initiated to correlate chemicals in the laboratory air with photographic properties. Three coating sites are being monitored. Six analyses are

being performed: oxidants, nitrogen dioxide, halogens, hydrogen halides, hydrogen selenide/hydrogen telluride, and arsenic/selenium/tellurium. This complete program was carried out for seven consecutive working days in the latter part of December. The results have not yet been received from National Loss Control Corporation, Long Grove, Illinois.

Unfortunately, films made on those seven days were all satisfactory. It was decided to delay further air sampling until there is a period when less than optimum films are produced. We are equipped to sample an additional eight days. The level of laboratory activity and contaminant generation is expected to rise after January 1st.

Three additional tests were run for nitrogen dioxide while nitric acid was in use for cleaning fritted glassware. It is suspect in the occasional failure to purify  $\text{CBr}_4$ .

The spent charcoal filters from the Barnebey-Cheney air purifier were also sent to the same analytical laboratory to identify major chemicals which may have been removed from the air. Tests requested were the six named above plus heavy metals and sulfur dioxide. The results have not yet been received.

### Film Studies

#### Polystyrene Binder:

Because the supply of MX4500 Polystyrene is no longer available, suitable substitutes have been tested as a replacement. Two Dow polystyrenes, Styron 685 and Styron 686, closely resemble the physical makeup of MX4500 and behave very similarly. Initial film tests indicate that either material can be used as a suitable replacement. Stability and aging tests of the two new polystyrenes are now in progress.

#### Subbed and Unsubbed Mylar:

A preliminary study was made with subbed Mylar. The subbing (108863) was a polyester resin coated 0.02 mil thick.

A coating of standard 5/D7 benzene control on unsubbed Mylar gives the following results:

D <sub>max</sub>	2.14	$\gamma$	1.3
Base + Fog	.22	AEI	1.10
$\Delta D$	1.92	$\Delta T_r$	120 sec.

A coating of the same material on subbed mylar gives these results:

D <sub>max</sub>	2.46	$\gamma$	1.8
Base + Fog	.34	AEI	1.20
$\Delta D$	2.12	$\Delta T_r$	160 sec.

The results show longer development times with slightly improved net density for the subbed Mylar. One notable complication is the absorption of blue dye from the fix solution by the subbing layer. This can be prevented by using fresh fix solutions, but may not be a problem since it appears that only the uncoated subbing layer, i.e. subbing which has not been coated with the polystyrene layer, absorbs dye.

Printouts on subbed mylar gave the same results as those on unsubbed Mylar. Preliminary shelf life studies also show that there is no significant difference between subbed and unsubbed base.

#### N-oxide Study:

Various N-oxides have been substituted in equivalent amounts for 4PO in 5/D7. This is part of the screening program to establish a structure-activity relationship for N-oxides. It is expected that the identification of a structure-activity relationship will aid in elucidating the mechanistic role of the N-oxide. Ten N-oxides have thus far been evaluated; they are: N2, N3, N5-11 and N15.

Compounds N5 and N6 gave films which were as good, if not slightly better than the normal standard 5/D7 benzene system. At present, optimization studies of the materials have not been completed.

Compounds N2 and N3 gave films which had lower maximum densities (.87 and 1.26) and higher fog levels (.45 and .86) than the standard control. A question, however, arose as to the purity of the sample. Further purification and drying of the samples will be undertaken and the samples re-evaluated.

Compound N10 (10 mg) gave a film whose image developed too rapidly (development time 50 sec.) resulting in excessive blotching. Lowering the amounts (5 and 2.25 mg) resulted in fogged films which gave no image at all.

The others (N7, 8, 9, 11 and 15) gave only fogged films with no discernible image.

#### Antioxidants:

Five antioxidants were added to the standard 5/D7 benzene system with the idea that shelf life stability might be enhanced and that photographic speed might be increased. Test results are as follows:

A) Plastanox 2246 - The maximum amount of Plastanox which can be added to the system without changing its photosensitivity was found to be 100  $\mu$ g. Decreasing the amount to 10  $\mu$ g resulted in no change from the control. Speed decay was not affected by addition of this material to the 5/D7 benzene system.

B) 2,4-Di-t-amylphenol - Addition of this material (5, 10  $\mu$ g) to the system gave lower maximum density (1.05 - 1.32) and slightly higher fog levels (.30 - .34) with longer development times than the standard control. Increasing the amount (10 mg) afforded no image at all after 600 sec. of development. Speed decay was not affected by addition of this material.

C) Santowhite - addition of this material (1 mg and 10, 100  $\mu$ g) to the system gave lower maximum density (1.30 - 1.58) and slightly higher fog levels (.30 - .37) than the standard control (maximum density 2.20, fog level .27). Speed decay also was not affected by addition of this material.

D) Santonox R - The maximum amount of Santonox R that can be added to the 5/D7 benzene system without changing its photosensitivity was found to be 10  $\mu$ g. Increasing the amount (1 mg, 100  $\mu$ g) gave lower maximum density (1.76, 1.60) and higher fog levels (.82, .36) with higher development times than the standard control. Speed decay was not affected by addition of this material.

E) 2,6-Di-t-butylphenol - The maximum amount of this material that can be added to the 5/D7 benzene system without changing its photosensitivity was found to be 100  $\mu$ g. Increasing the amount (1 mg) afforded no image at all after 1020 seconds development time while decreasing the amount (10  $\mu$ g) resulted in no change from the control. Speed decay also was not affected by addition of this material.

### Pilot Coating

With the termination of the pilot coating effort on December 31, speeds in excess of the 2.0 objective had been realized. On two separate coatings performed on different days, speeds of 2.3 and 2.2 were obtained. The D-log E curves are illustrated in Figures 3 and 4.

The November results, which were discussed last month, had indicated the feasibility of attaining the desired objective. The November report also discussed the need for increased uniformity and increased development temperature if higher speeds were to be realized. Temperature in the processing lab was correspondingly increased from 60°F to 70-72°F (Note ERROR: last month's report described these temperatures as °C, they should read °F).

A series of experiments performed by the coating staff demonstrated that static electricity was a prime cause of coating nonuniformities. The existing coating equipment limited the corrective measures which could be taken, however, some quick fixes were made that reduced the static problem. This was achieved by raising the humidity as high as possible (50 grains at 65°F) and by positioning two polonium antistatic bars (3M) above the web immediately fore and aft of the coating head.

Having taken these corrective measures, a total of 10 coating runs were made. The results are summarized in Table 1 and as follows:

- Run 325082 - An AEI of 0.77 (Figure 1) marked a significant improvement upon previous results. The improvement was attributed to better coating uniformity, improved handling techniques and a higher processing temperature (70-72°F).
- Run 325-83 - Excellent uniformity attributed to lessened static due to presence of 20% tetrachloroethylene ( $C_2Cl_4$ ) as co-solvent (see Figure 2).
- Runs 325085, 086 - Coating variations were significant and sufficient to produce premature blotching, thereby preventing sufficient development for the realization of high speeds.
- Run 325087 - Same as -083 but with 40%  $C_2Cl_4$ . Development resulted in extensive fogging. Lab experiments indicate contamination of  $C_2Cl_4$  and not its higher concentration as the cause of fogging.
- Run 325088 - Same as 325085 and -086.
- Run 325091 - Coating uniformity was fairly good. Depending upon the uniformity of individual pieces, speeds from 0.27 to 2.3 (Figure 3) were obtained.
- Run 325092 - Coating uniformity poor. This run was made immediately after -091. The poor quality was believed associated with improper cleaning and/or handling of the slot tube (see also -094).
- Run 325093 - Same as -091; high speed of 2.2 (see Figure 4).
- Run 325-94 - Same as -092.

  
Conclusions

The ninety day pilot coating effort demonstrated the capability of P325A material (5/D7) to be machine coated on a preliminary basis while retaining the sensitivity demonstrated by hand coatings.

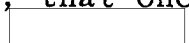
The results of machine coating parallel those which have been attained throughout with hand coatings, with the exception of thickness variations. In fact, machine coating variations are currently more pronounced than hand coated variations. These thickness variations resulted in a more rapid onset of blotching than is usual for hand coatings, and appear to have prevented the realization of more AEI's in the range of 2.3 as well as still higher speeds.

The speed decay phenomenon necessitated immediate sensitometric evaluation which in turn limited the number of evaluations which could be made, as well as the lengths which could be practically coated. Also, speed decay severely limits the time which can be allotted for drying. The film could not be wound and therefore, only short runs (5-30 ft.) were practical. Short runs were further necessitated by the shortage of D260. It is the consensus of the coating staff that many of the observed coating defects and especially thickness variations, will be less apparent with longer runs.

A number of defects can be attributed to the use of unsubbed Mylar. Unsubbed Mylar was used exclusively for this ninety day effort, and to date has been used exclusively for laboratory research.

Comparison of run 325092 with -091 and -094 with -093 also indicate that gross thickness variations can be attributed to improper cleaning and/or handling of the coating head, but the critical factors were not determined.

Regular coating patterns such as chatter are known to be associated with various mechanical shortcomings of the existing installation. Appropriate modification of this installation will reduce or eliminate these patterns.

Having recognized the progress which was associated with the ninety day coating effort, it can be concluded, that once the problem of speed decay is in hand, high speed,  Free Radical camera materials would present those complications normally associated with the coating of any highly sensitive film material.

25X1

  
**PROBLEMS**

Chemical Samples Company's delivery of poor quality D260 prime dye materials.

**FINANCIAL**

All project funds expended on December 31, 1971 proposal submitted for follow-on program.

**PLANS FOR NEXT REPORTING PERIOD**

- 1) Continue project effort; awaiting approval for follow-on.
- 2) Bear on chemical contamination as a factor in shelf life/speed decay.
- 3) Continue engineering support of the chemistry program.
- 4) Push for identification of the isolated impurities from the prime materials.

TABLE 1

Run	Viscosity (cps)	Coating Speed (fpm)	Oven Zone (°F)			Pattern	AEI Printout	AEI Developed	Figure	Comments
			1	2	3					
325082	-	17.0	off	off	65	good	-	0.77	1	
-083	11.5	"	"	"	"	excellent	-	0.62	2	20% C
-085	-	"	"	"	"	fair	2.2 10 <sup>-4</sup> (1 hr)	-	-	blot sens. good
-086	-	"	"	"	"	"	1.4 10 <sup>-4</sup> (1 hr)	-	-	blotching, sens. good
-087	13.0	"	"	"	63	excellent	-	-	-	40% C <sub>2</sub> Cl <sub>4</sub> fogging
-088	-	"	"	"	"	poor	-	-	-	extensive blotching
-091	-	"	"	"	65	good	-	2.3	3	-
-092	-	"	"	"	"	poor	-	-	-	blotching, no measurable results
-093	-	"	"	"	43	good	-	2.2	4	-
-094	-	"	"	"	60	poor	-	-	-	blotching, no measurable results

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25X1

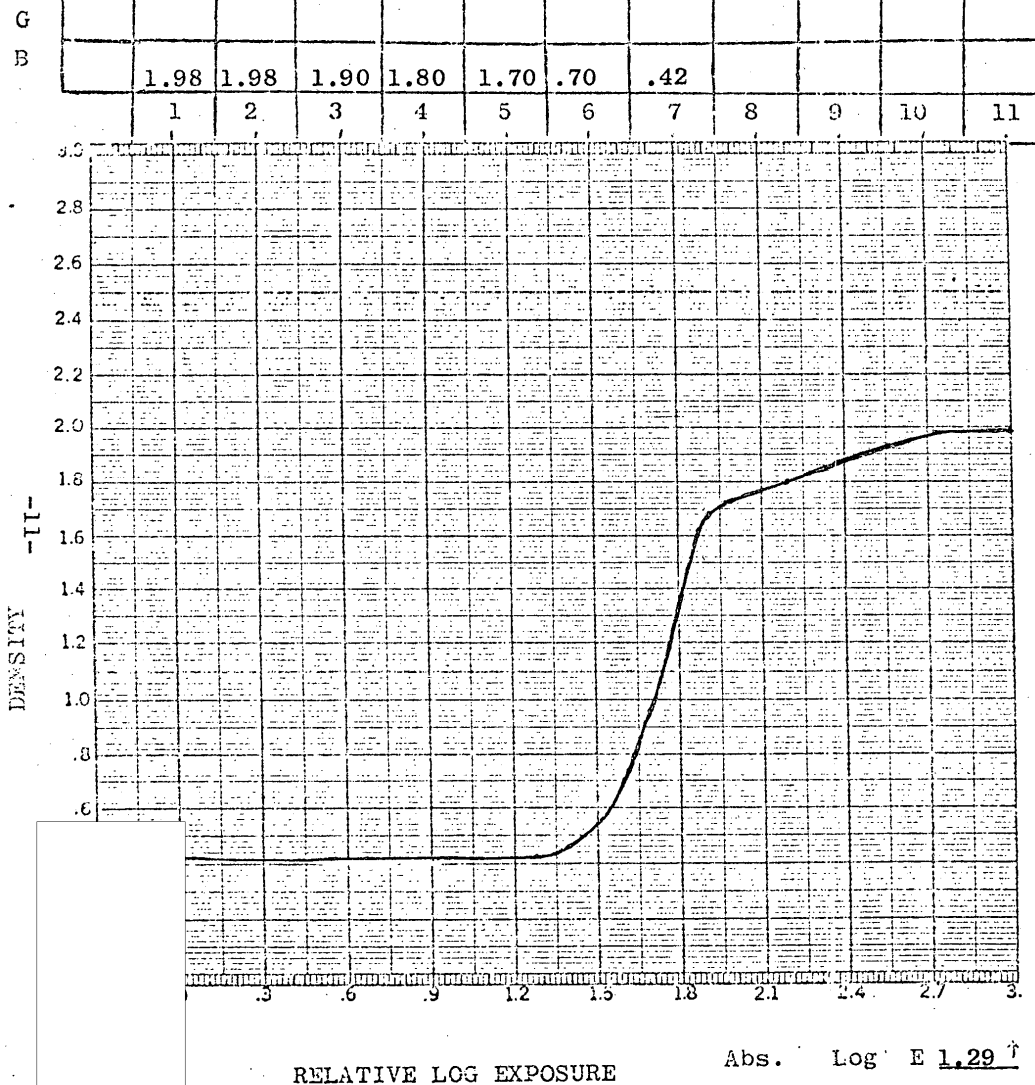


FIGURE 1

5/D7 (Benzene)

RUN 325082

DEVELOPED

25X1

EXPOSURE STATION: H101

INTENSITY: 215 mc

EXPOSURE TIME: .09 sec.

E EXPOSURE: 19.4 mc sec.

Log EXPOSURE: 1.29

RED LITE STATION: HID-2 LAMP:

STATIONARY PLATEN: X OSCILLATING:

RED LITE DEV. TIME: 68 sec.

TIME/PASS:

FILTERS USED: N.D.:

RADIATED POWER:

ROOM TEMP: 68°

HUMIDITY:

PLATEN TEMP:

25X1

γ = 3.2

AEI: .77

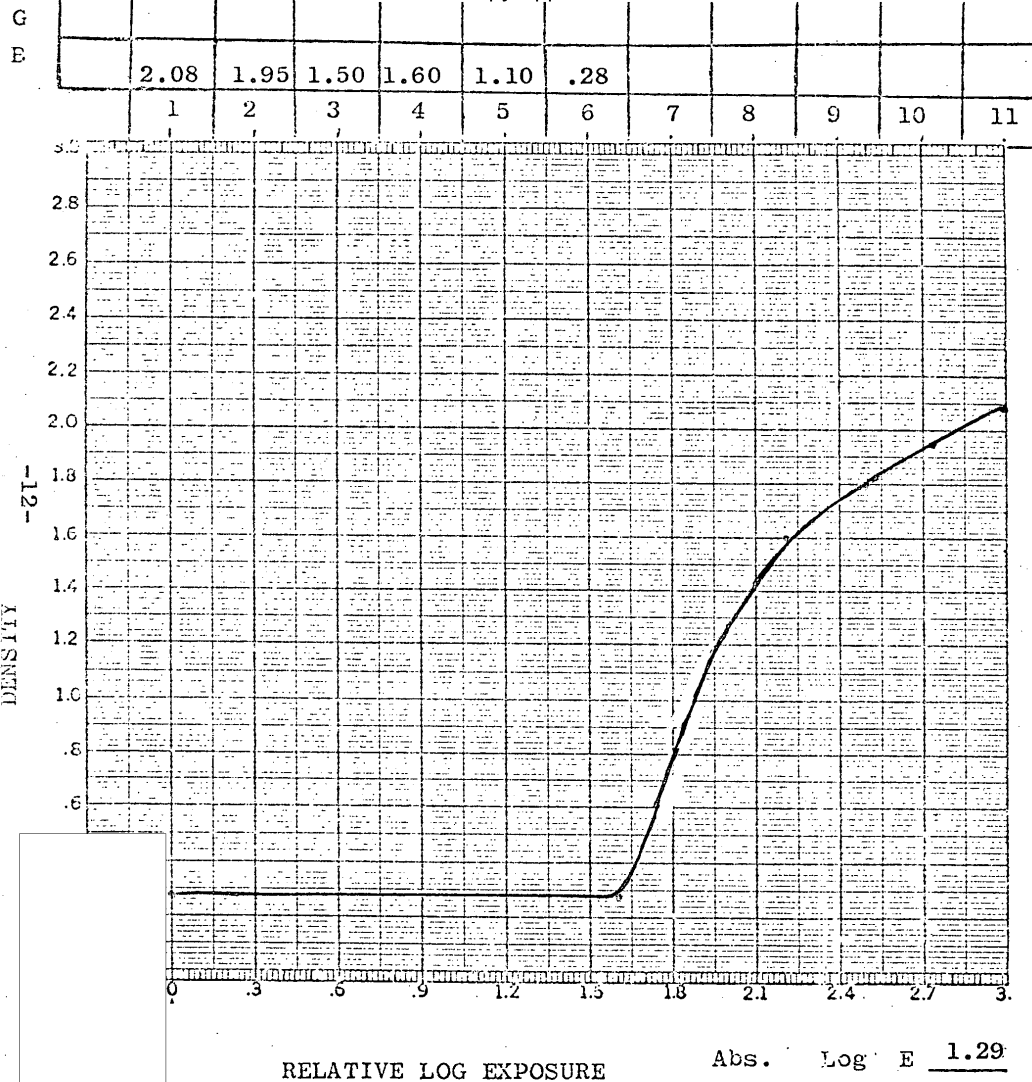


FIGURE 2  
5/D7 (Benzene-20%  
RUN 325083  
DEVELOPED

EXPOSURE STATION: H101  
INTENSITY: 215 mc  
EXPOSURE TIME: .09 sec.  
E EXPOSURE: 19.4 mc sec.  
Log EXPOSURE: 1.29

RED LITE STATION: H102 LAMP:  
STATIONARY PLATEN: X OSCILLATING:  
RED LITE DEV. TIME 90 sec.  
TIME/PASS:  
FILTERS USED: N.D.:  
RADIATED POWER:

ROOM TEMP: 68°  
HUMIDITY: 25X1  
PLATEN TEMP:

$\gamma = 2.6$   
AEI: .62

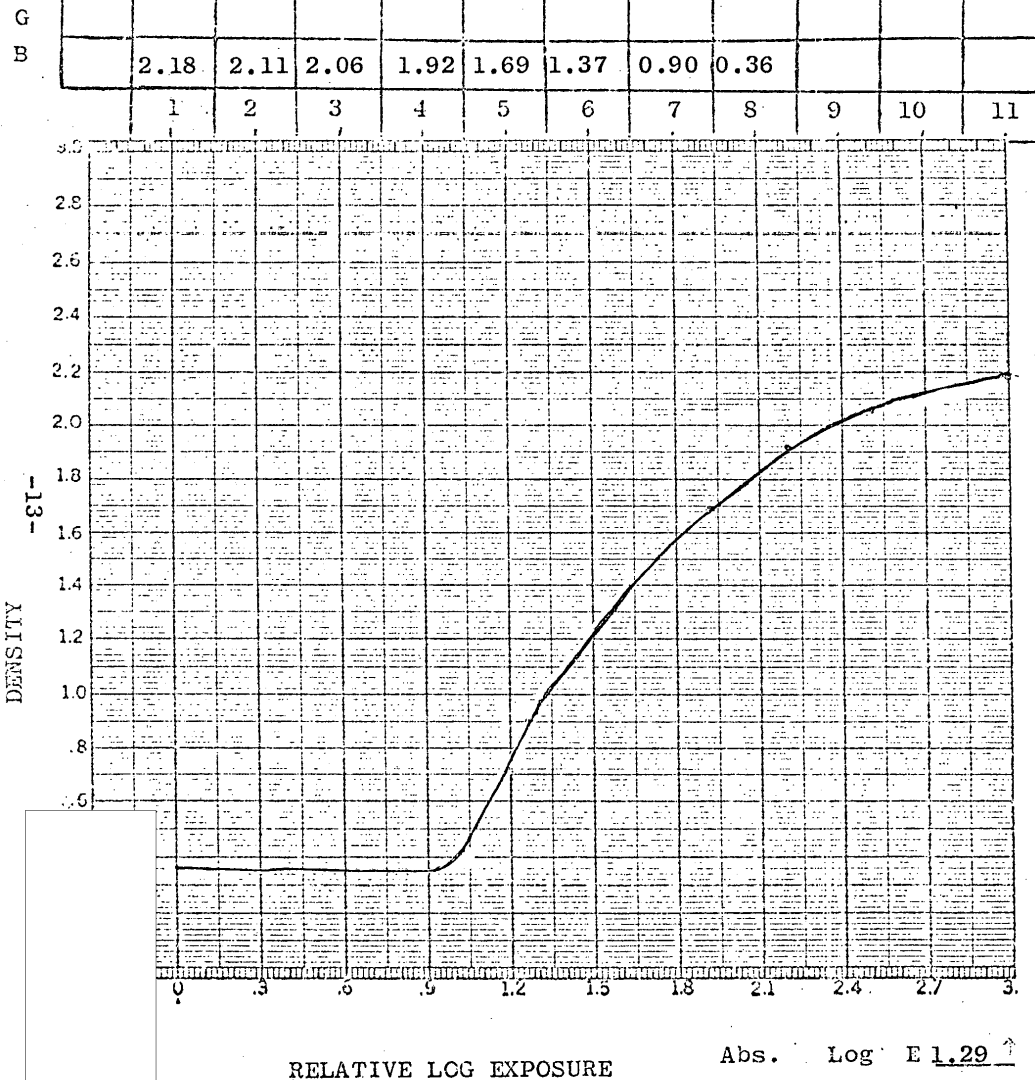


FIGURE 3  
5/D7 (Benzene) 25X1  
RUN 325091  
DEVELOPED

EXPOSURE STATION: H101  
INTENSITY: 215 mc  
EXPOSURE TIME: .09 sec.  
E EXPOSURE: 19.4 mc sec.  
Log EXPOSURE: 1.29

RED LITE STATION: H102 LAMP:  
STATIONARY PLATEN: X OSCILLATING:  
RED LITE DEV. TIME: 94 sec.  
TIME/PASS:  
FILTERS USED: N.D.:  
RADIATED POWER:

ROOM TEMP: 68°  
HUMIDITY:  
PLATEN TEMP:

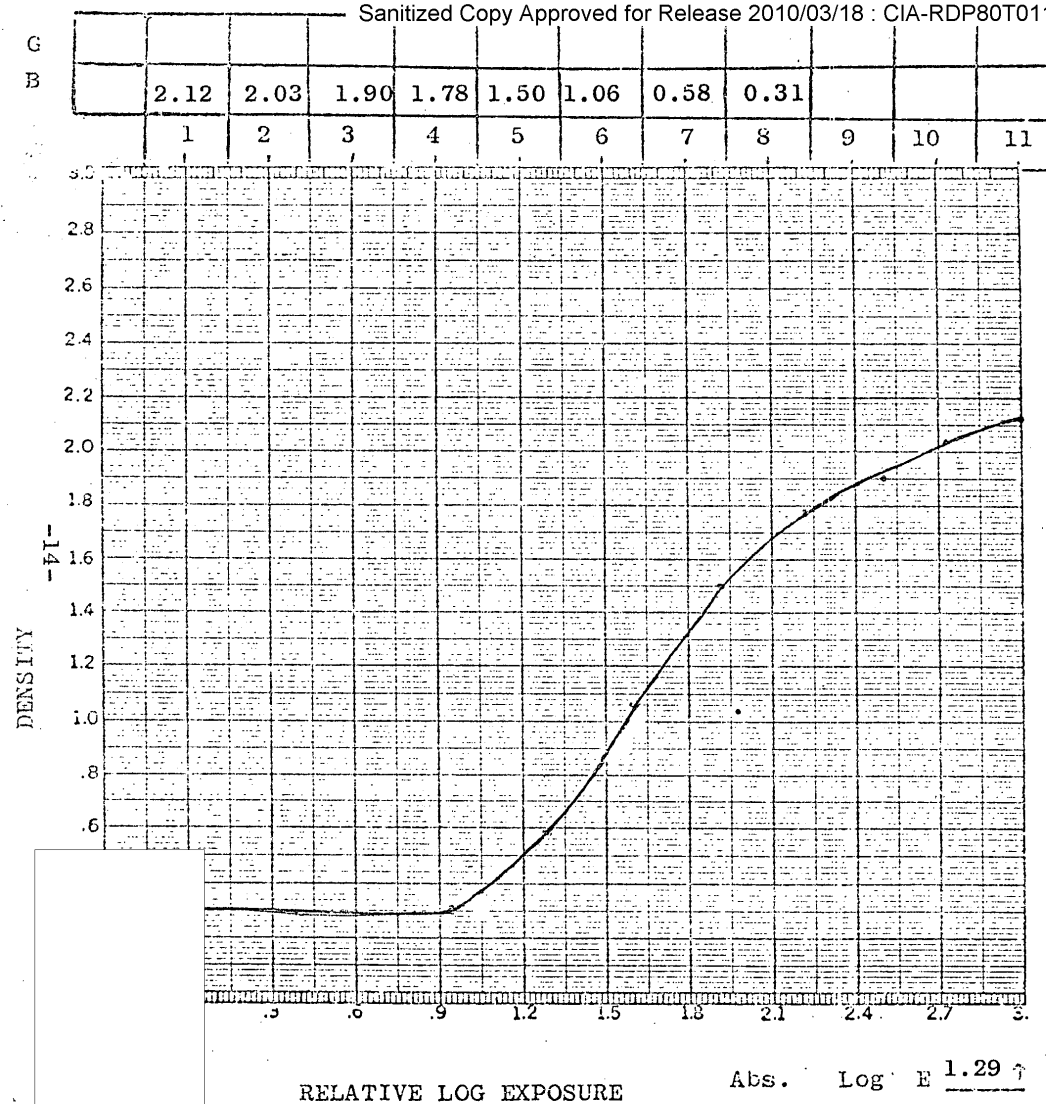
$\gamma = 1.6$   
AEI: 2.3

5/D7 (Benzene)

RUN 325093

DEVELOPED

25X1



EXPOSURE STATION: H101

INTENSITY: 215 mc

EXPOSURE TIME: .09 sec.

E EXPOSURE: 19.4 mc sec.

Log EXPOSURE: 1.29

RED LITE STATION: HID-2 LAMP:

STATIONARY PLATEN: X OSCILLATING:

RED LITE DEV. TIME: 60 sec.

TIME/PASS:

FILTERS USED: N.D.:

RADIATED POWER:

ROOM TEMP: 68°

HUMIDITY:

PLATEN TEMP:

25X1

 $\gamma = 1.6$ 

AEI: 2.2

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